

The University of Chicago

THE FREEZING POINTS
OF AQUEOUS HYDROCHLORIC ACID
SOLUTIONS ONE-TENTH
TO FOUR MOLAL

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By

WALTER JAMES WYATT, JR.

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I. INTRODUCTION

The requirements for the precise calculation of activity coefficients from freezing point and thermal data have been discussed by Young,¹ and a study of the literature has revealed that the freezing point depressions, as well as the thermal data deserve further attention. In the review by Randall and E. Young² of the hydrochloric acid literature which pertains to the calculation of activity coefficients, the need for more accurate freezing point data for concentrations beyond one molal seems especially marked. Their calculations extend only that far. Two reports have been made of measurements on hydrochloric acid with modern technique: That of Randall and Vanselow³ who employed the differential method in their study of dilute solutions up to 0.1 molal and that of Chadwell⁴ who made use of a platinum resistance thermometer as a temperature measuring instrument in a single freezing point vessel.

Urbain⁵ and Young in their work on the freezing points of concentrated sodium chloride solutions found that a technique different from that employed with dilute solutions is required for accurate work on solutions more concentrated than one molal. It

¹T.F. Young, Chem. Rev., 13, 103 (1933).

²Randall and E. Young, J. Am. Chem. Soc., 50, 989 (1928).

³Randall and Vanselow, J. Am. Chem. Soc., 46, 2418 (1924).

⁴Chadwell, J. Am. Chem. Soc., 49, 2795 (1927).

⁵Urbain, Ph. D. Dissertation, University of Chicago (1934).

is the purpose of this investigation to make a further study of the factors involved in accurate measurements on moderately concentrated solutions, and to obtain data for 0.1 to 4.0 molal hydrochloric acid. These, in conjunction with values for the relative heat contents, will make possible the direct comparison of activity coefficients calculated from electromotive force⁶ and freezing point data. The former coefficients are probably very precise except at high concentrations, and, since those based on vapor pressure measurements are precise only at high concentrations, it is desirable to obtain values of high precision by the freezing point method in the intermediate range.

A simple outline of the equilibrium method for obtaining freezing point depressions is: (1) to obtain an equilibrium mixture, (2) to measure its temperature, and (3) to analyze the liquid phase. Our description of the apparatus and procedure will be from the point of view of the objects to be attained.

II. THE EQUILIBRIUM MIXTURE

What is really meant by the expression, equilibrium mixture, from the view point of actual practice, is an approach to this ideal state within the detecting sensitivity of instruments. Obtaining a reproducible equilibrium temperature with the required precision is not so simple a matter as many have assumed, even in the reference vessel,⁷ and in the ice-solution vessel the difficulty is magnified many times due to the change in concentration produced by melting or freezing of ice. The various factors which contribute to the alteration of the conditions within the vessels can best be handled in a differential apparatus where all but the

⁶Harned and Ehlers, J. Am. Chem. Soc., 55, 2179 (1933).

⁷White, J. Am. Chem. Soc., 56, 20 (1934).

one effect to be measured can be made negligible, or closely matched, and where all the advantages of using a thermel as a temperature measuring instrument may be realized. The factors mentioned above which have an effect on the measured temperature may be summarized for the ice-solution vessel:

$$T = f(q, h, r, s/v, C_3, C_2)$$

and for the ice-water vessel:

$$T' = f(q', h', r', s'/v', C'_3)$$

$$T - T' = \Delta T$$

where q is the total heat gained per minute as heat of stirring, conduction through the thermel, the connecting tubes and the walls of the dewars, and by way of the air stream; h , the height of liquid in the dewars; r , the rate at which the liquid is made to circulate; (s/v) , the ratio of ice surface to the volume of liquid; C_3 , the concentration of the dissolved gases; C_2 , the concentration of the solute studied.

Since the contribution of q and q' to ΔT cannot be reduced to zero even though they are made equal, the apparatus is designed to make them negligible, in other words, to establish an approximately adiabatic condition for each half. Either the heat of stirring must be reduced to a low value, or it must be off-set by conduction through the metal dewar containers, the connecting tubes and stirring rods. The latter alternative is objectionable because it would cause melting and re-freezing of ice and thereby produce a greater tendency to form channels through the ice. The former has been adopted for this work. Presumably, the best stirring is that resulting in a relatively high ratio of volume circulated past a given horizontal plane to calories introduced thereby. This implies that turbulent flow will be reduced as much as possible. The stirrers chosen, and described below under the

section called "Freezing Point Assembly," seems to fulfill this requirement more satisfactorily than the other types which were considered. The thermal leakage between the vessel and its surroundings was reduced to a low value by providing each half of the apparatus with a separate bath whose temperature was maintained within one degree of that in the vessel except for the most concentrated solutions.

There must be a value of (s/v) , all the other factors being constant, below which a satisfactory equilibrium mixture cannot be obtained. This value would become smaller as q is diminished. The test for the establishment of an equilibrium condition, as described in section V, would indicate whether too low a value of (s/v) actually obtains. The equilibrium condition as indicated by this test was satisfactory even when the amount of ice was reduced to about one-half the usual quantity, and in any actual determination the amount was never less than this.

The effect of the difference in pressure on the equilibrium temperature at the top and bottom of the vessels has been discussed by Scatchard, Jones and Prentiss⁸ and also by Robertson and LaMer.⁹ They have calculated a difference of about 0.00016° between the equilibrium temperatures at the top and bottom of a column of water twenty centimeters high. The temperature observed at any point is a mean value, and its relation to the equilibrium temperature at that point depends on the stirring and (s/v) . In dilute solutions any great difference in the rate at which the liquids circulate, in the packing of the ice and in the height of the liquids would cause an appreciable error due to this pressure

⁸Scatchard, Jones and Prentiss, J. Am. Chem. Soc., 54, 2676 (1932).

⁹Robertson and LaMer, J. Phy. Chem., 35, 1953 (1931).

difference. The magnitude of the error introduced by this pressure effect will be the smaller, the more closely the factors, h , r , and s/v , are matched in the two halves of the apparatus. A consideration of the construction and use of our apparatus will make it clear how the difference in temperature due to a difference in pressure is made very small.

Since the concentration of dissolved air in water at zero degrees is 0.001 molal, its effect on ΔT cannot be neglected in measurements on dilute solutions. The majority of the modern investigators have made the assumption that the contribution of the gas to the freezing point depression is proportional to its concentration. Scatchard and his co-workers¹⁰ have given a more complete treatment of one aspect of the problem, namely, the salting-out effect. They make two reasonable assumptions: (1) Henry's law is obeyed at any one salt concentration, and (2) "the change in chemical potential of the gas is proportional to the salt concentration at constant mol fraction of the gas." They calculate the error to be smaller than the experimental error at all concentrations provided the contents of both vessels are within one per cent of saturation with respect to air. Their calculation is admittedly incomplete because they neglect the effect on the solubility of the lower temperature of the working side. This effect is just the opposite of that for which the calculation is made and may well reduce the error to zero, or even change the sign. Scatchard's theory modifies somewhat the effect which has been usually assumed in that it reduces the magnitude of the error, but it does not permit a quantitative estimate of the total effect. The available data¹¹ on air solubility in hydrochloric acid

¹⁰Scatchard, Jones and Prentiss, loc. cit.

¹¹"International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, 1928, p. 258.

solutions does not allow a quantitative estimate of the contribution of the air solubility to ΔT , but extended extrapolations of the oxygen solubility data indicate that the mol fraction of oxygen in four molal hydrochloric acid at its freezing point is only slightly smaller than that in water at zero degrees. If Scatchard's second assumption holds here, the error with oxygen would probably be in the opposite direction from that usually assumed. But in any case the assumption seems justified that the error in the observed freezing point depression due to a difference in the effect of the air in the two vessels is negligible provided both vessels are saturated to the same degree, or within 5 per cent of the solubility, when measurements are made on dilute solutions. A greater difference is permissible for measurements on more concentrated solutions. The above condition may be established easily when air is passed through the vessels. The time required to saturate water at zero degrees within 5 per cent of the solubility has been found by Becker¹² to be about ten minutes when the volume of water per square centimeter of surface exposed was one cubic centimeter.

The freezing point assembly.- The apparatus used by Urbain¹³ was modified as follows (see Fig. 1): (1) glass pump stirrers, A, mechanically operated, and tantalum hand stirrers, B, were used in both dewars; (2) paraffined corks, C, furnished additional thermal insulation and also prevented hydrochloric acid splashes from reaching the brass parts; (3) protective glass tubes, E, held in place by short lengths of rubber tubing, G, were placed within the brass tubes, D, and extended all the way through the corks, C; (4) an arrangement to saturate the contents of both

¹²Becker, J. Ind. Eng. Chem., 16, 1220 (1924).

¹³Urbain, loc. cit.

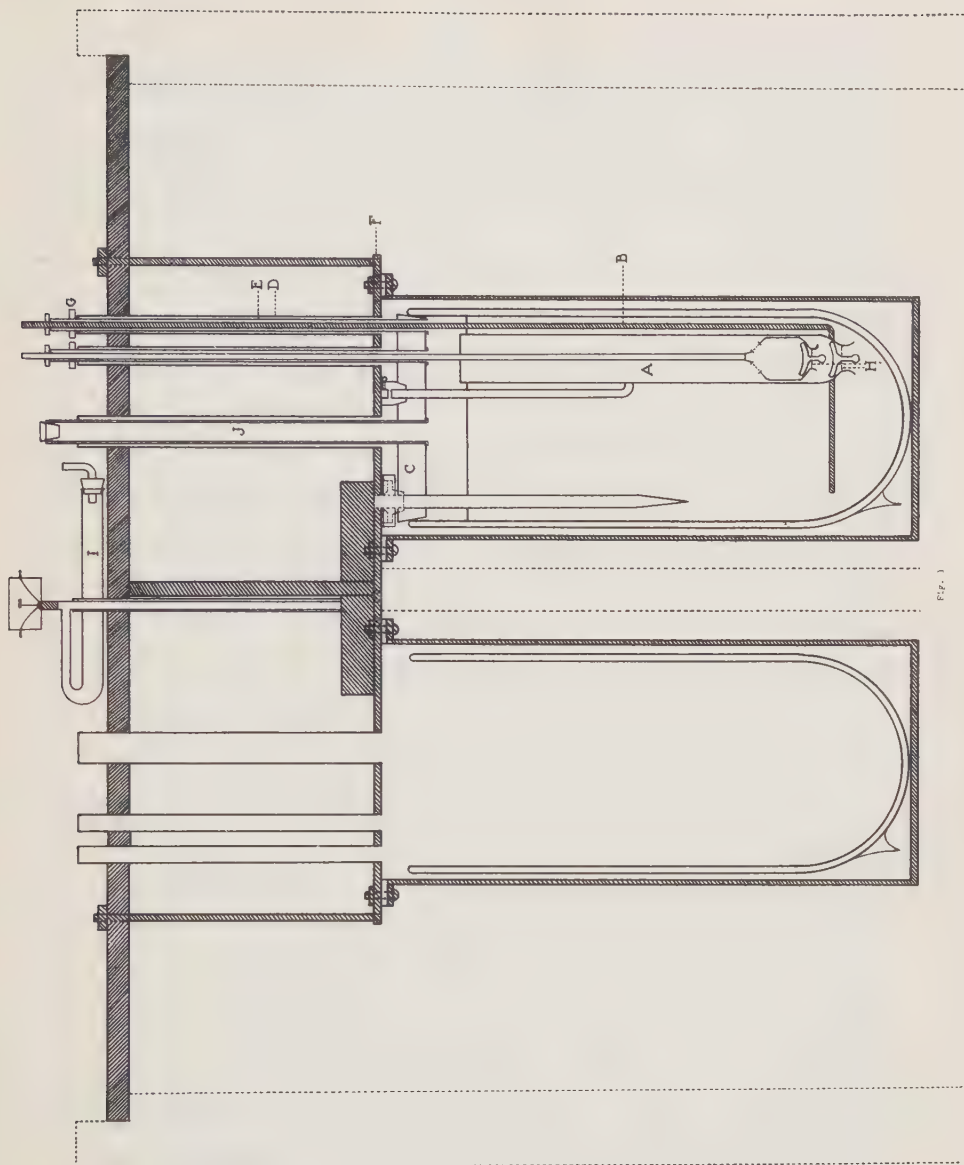


Fig. 1

dewars with cooled, purified air drawn in from outside the laboratory was added to the equipment; (5) better insulation for the containing baths; (6) a new thermel provided with a drying tube containing phosphorous pentoxide; (7) an oil thermostat for the Mueller Bridge to replace the air thermostat; (8) a fine adjustment lever for the Bridge slide wire which held the dial at a given setting more firmly than heretofore.

The first of the changes was adopted after a study of the merits of various methods for continually renewing the liquid-ice surface. Either the liquid or the ice must be put into motion, and the usual procedure has been to circulate the liquid with stirrers of the propeller type, the air lift type or the valve-pump type. The last named type, as employed by Scatchard, Jones and Prentiss,¹⁴ seems to be the best fitted to meet the requirements in dilute solutions of salts. In our work several arrangements were designed and tested for moving the ice through the liquid but none proved entirely satisfactory. After it was demonstrated that efficient valve-type pumps could be made of glass and a short length of tantalum or platinum wire, they were adopted in our work. The main advantages are a uniform circulation of the liquid which is practically independent of the viscosity, and presumably less heat of stirring per volume of liquid circulated. The flow is less turbulent than that produced by propellers. The cylinders, plungers, valves, and rods were made of glass. The ice screens and valve stops, H (Fig. 1) were made of tantalum wire. The valves were free to move vertically about a quarter of an inch, and from Fig. 1 it is obvious how these operated and how pumping was effected by the up and down stroke of the rod and plunger. The efficiency and smoothness of

¹⁴Scatchard, Jones and Prentiss, loc. cit.

operation were good provided the plungers were properly shaped and the cylinders carefully aligned. The shape found to be best is indicated in the diagram. The two pumps were made as nearly alike as possible and were operated simultaneously by clamping the glass rods, protected by rubber, into brass connections and these, in turn, were connected to the ends of a cross arm on a lever. In this way one up and down motion of the lever operated both stirrers. Approximately fifty cubic centimeters of liquid were circulated in each vessel at every stroke, and, provided no "channels" through the ice were formed, all of the liquid passed through the cylinder about six times every minute when the pump operated at the usual rate of sixty strokes a minute.

The tantalum hand stirrers were shown to be a necessary part of the freezing point assembly because of: (1) the tendency of the ice lumps to freeze together at the top of the ice-water mixture, and thus reduce the ice surface, and (2) the ice in the ice-solution mixture to allow the formation of channels. The freezing of any liquid freshly pumped from the bottom where the freezing point is lower could account for the first effect. Also the slight lateral pressure on the lumps packed together would cause some melting and refreezing.

Air for saturating the dewar liquids was drawn from outside the laboratory with an ordinary filter pump, whose lower end passed through a rubber stopper into an aspirator bottle. The pressure created upon separation of the water and air was sufficient to force the latter through the train into the apparatus. The purification train consisted of soda-lime towers, a y-tube to divide the stream, dilute sulfuric acid wash bottles, and finally gas wash bottles one-third filled with lump ice prepared as for freezing point measurements and placed in the reference thermostat.

This reduced the temperature of the air to zero just before it passed into the dewars. Glass tubes through J in Fig. 1 conducted the air into the liquid ice mixtures.

The containing baths which Urbain¹⁵ used were furnished with additional insulation to the extent of two layers of "cellotex" on the sides and a removable top (not shown in Fig. 1) having three layers of the same material, and made in two parts which fitted around the projecting tubes and thermel terminal. The containing bath for each dewar should provide an environment such that the heat loss is approximately the same as that gained by stirring and unavoidable conduction. It was found that if the bath temperature was kept one degree warmer than that in the ice-solution vessel after it had been stirred sufficiently to establish approximately equilibrium conditions, the change in the observed temperature, when the concentration was two molal, amounted to about 0.0007 per cent of the lowering per minute. For concentrations greater than three molal, the bath temperature was kept within one degree of that of the freezing point vessel contents. For measurements on the most concentrated solutions the two temperatures could not be made to match very closely throughout the process of attaining equilibrium and withdrawal of the sample, but in no case did the reading change more than 0.02 per cent of the depression, while the sample was being withdrawn. In order to maintain the proper temperatures in the reference bath and the sub-zero bath, mixtures of water and ice and calcium chloride and ice were used, respectively. A very efficient stirrer on each side circulated the liquid through the ice.

That fraction of q contributed by the air stream is

¹⁵Urbain, loc. cit.

estimated to be 0.1 calorie per minute at -15 degrees. This can melt approximately 0.0002 grams of ice and change the concentration to the extent of 0.0001 per cent.

Aside from the melting of the ice, the only factors affecting the constancy of C_2 which need to be considered are the condensation or evaporation of water or the evaporation of hydrochloric acid. The air stream entering the freezing point vessel is approximately saturated with water vapor at zero degrees and a large fraction may condense into moderately concentrated solution-ice mixtures. At the rate of thirty cubic centimeters of air per minute, a calculation shows that only 10^{-6} gram of water can condense per minute when the air temperature is reduced to that of the vessel contents. An estimate of the evaporation at the top of the vessel is harder to make, but it cannot be large even on the driest days because circulation of air down the tubes is prevented by the air stream. That the error due to evaporation of hydrochloric acid is also negligible can be shown as follows: At four molal the vapor pressure of hydrochloric acid is 2.46 times 10^{-5} atmospheres.¹⁶ Provided that the air stream becomes saturated and that the perfect gas law holds, only 4 times 10^{-8} mols evaporate per minute, a simple calculation shows that the combined effects of water condensation and hydrochloric acid evaporation cannot change the temperature by more than 0.00001 per cent of the depression per minute.

III. MEASUREMENT OF THE TEMPERATURE

Of the two instruments, the thermel and the platinum resistance thermometer, used in modern technique to measure small temperature differences, the thermel appears superior in three respects: electromotive force readings present fewer difficulties

¹⁶Bates and Kirschmann, J. Am. Chem. Soc., 41, 1991 (1919).

than resistance readings; the ordinary thermel has about ten to fifty times the sensitivity of the platinum thermometer;¹⁷ and certain effects can be balanced in differential measurements more satisfactorily than they can be corrected for in measurements with a platinum thermometer. Although the thermel is often calibrated with the other instrument, the nature of the calibration makes the second advantage quite real.

The copper-constantan thermel employed in this work consisted of twenty-four elements made of No. 32 copper and No. 26 constantan wire, doubly insulated with cotton and silk respectively. The leads were such that the two halves could be used in opposition, in series, or independently. The testing of the wire and the construction were according to the methods of White¹⁸ with a few minor modifications.¹⁹ The thermel case was essentially the same as that used by Wampler²⁰ and by Urbain,²¹ but it was found necessary to make it much less susceptible to the entrance of moisture. The joint in the brass box which enclosed the middle portion was sealed with litharge and glycerine suitably supported. The whole box and the tube for the leads were given three coats of "glyptal" lacquer.²² The joints between the glass "leg-casings" and the brass cover were made very sturdy with special rubber

¹⁷Chadwell, loc. cit., claims a reading precision of 5×10^{-4} degrees for his platinum thermometer.

¹⁸White, J. Am. Chem. Soc., 36, 2292 (1914).

¹⁹The junctions were coated with "sealo," a preparation of the General Chemical Company, Chicago, Illinois. This was found not to be appreciably affected by the molten naphthalene in which they were immersed.

²⁰Wampler, Ph. D. Dissertation, University of Chicago, 1931.

²¹Urbain, loc. cit.

²²A product of General Electric Supply Company, Chicago, Illinois.

gasket arrangements. The four lead wires emerged from their exit tube into the bakelite head through a thick piece in seal. Just below this seal there was a side arm connected with a phosphorous pentoxide drying tube which, in turn, was open to the air. This kept the pressure the same as that of the atmosphere at the low temperatures of the measurements without any intake of moist air. A good test of moisture in the thermel case is a measurement of the resistance between the halves of the thermel. According to White²³ a resistance of 10^7 ohms or greater should obtain in the most precise measurements of electromotive force. This test was made before and after every run and no readings were taken nor values accepted, respectively, unless the test was favorable. On several occasions moisture had entered, but it was found that the evacuation of the case for ten minutes and then the admission of air were sufficient to raise resistance higher than 10^8 ohms, the maximum which could be measured on the instrument used.

The electromotive force of the thermel was measured with a White potentiometer, having a range of 0.0 to 0.1 volt, and a Leeds and Northrup type HS galvanometer, having a resistance of forty ohms, period 4.9 seconds, external critical damping resistance of 260 ohms, and a sensitivity of 2.84 mm. per microvolt at four meters, the actual scale distance. This sensitivity translated into degrees means that the precision of a reading is 0.00005° per 0.3 of a mm. deflection. This would not be sufficient for very dilute solutions, but a higher precision is not needed to obtain an accuracy of a given percentage when measurements are made on more concentrated solutions. Furthermore, other factors limiting the precision of the determinations on solutions

²³White, J. Sci. Inst., 4, 142 (1933).

more concentrated than 0.1 molal make it impossible to take advantage of a higher sensitivity.

The electrical system was shielded and the metal supports connected as recommended by White.²⁴

To test for parasitic currents a copper coil having the same resistance was substituted for the thermel. Usually they were barely detectable if present at all. However, on several occasions when the weather was very damp measurements were suspended because of an electrical leak which was reduced but not eliminated by careful insulation. In dry weather this effect disappeared.

To obtain the full advantage of the thermel as an instrument for measuring small temperature differences it is necessary to make the calibration under conditions as nearly as possible identical with those of the freezing point measurements. The thermel was calibrated with a platinum resistance thermometer inserted through tubes, J (Fig. 1) first in the reference side to get the R_0 reading, and then in the other side. Readings were made of the electromotive force and the resistance while conditions, except for the substitution of sodium chloride solutions for hydrochloric acid and the presence of the thermometer, were just as in our freezing point measurements. The substitution of sodium chloride was made to prevent injury to the silver case of the thermometer. The errors in the platinum thermometer temperatures are relatively much greater near zero degrees and it seemed desirable to extend the calibration range to higher temperatures in order to interpolate through this region. To obtain these points the freezing point assembly was set up as usual except that water was substituted for the solution-ice mixture in the freezing

²⁴White, J. Am. Chem. Soc., 36, 1874 (1914).

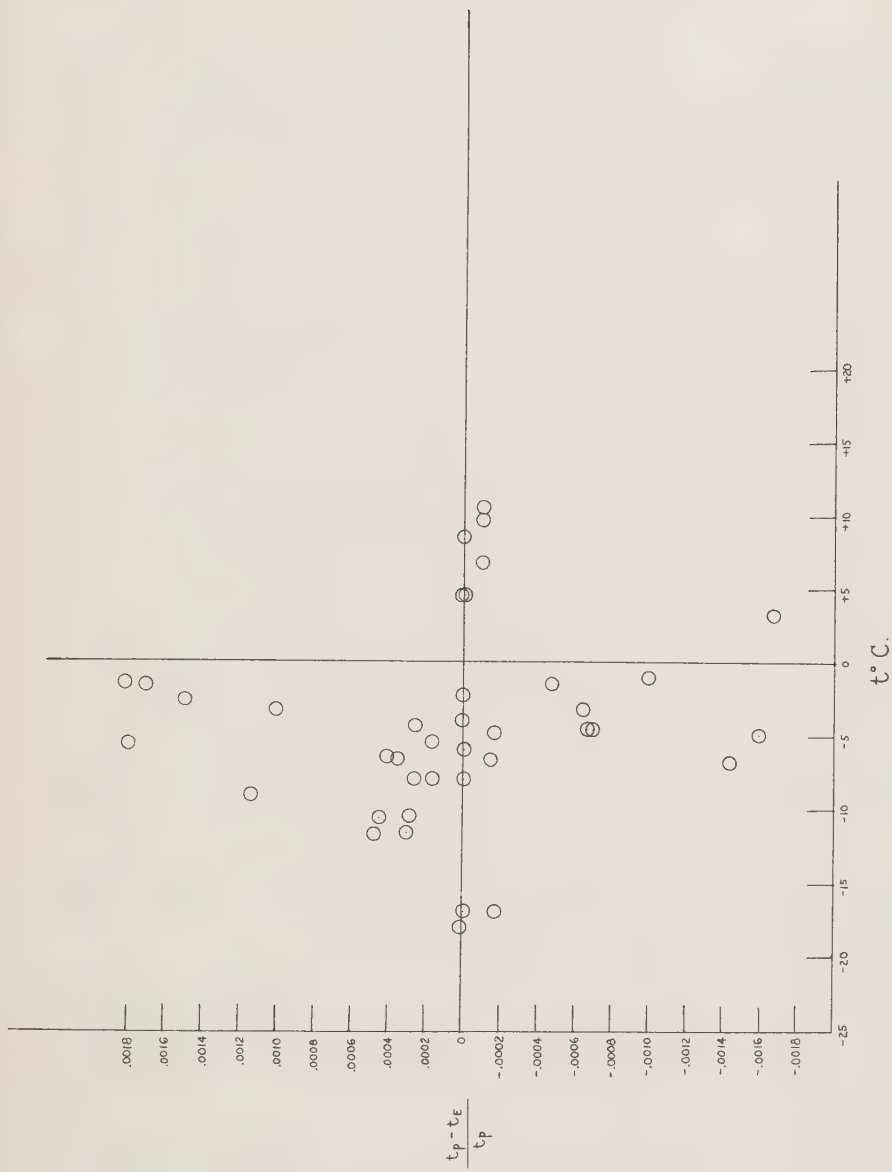


Fig. 2

TABLE I
THERMEL CALIBRATION

Point No.	Date	R -20	N -20	C	R ₀ or R _t	-10(R _t -R ₀)	k'	-t _p
IP	6/5	5.63866	5.63724	.00325	25.64052			
1	6/5		4.44580	.00317	24.44897	11.9155	.1858	11.7297
2	6/5		4.44590	.00317	24.44907	11.9145	.1858	11.7287
3	6/5		4.58683	.00315	24.58998	10.5054	.1636	10.3418
4	6/5		4.81933	.00315	24.82248	8.1804	.1233	8.0571
5	6/5		4.82091	.00317	24.82407	8.1645	.1231	8.0414
6	6/5		5.17338	.00324	25.17662	4.6390	.0676	4.5714
IP	6/7	5.63863	5.63723	.00327	25.64050			
7	6/7		3.80382	.00303	23.80685	18.3365	.3028	18.0337
8	6/7		3.82275	.00306	23.82581	18.1469	.2992	17.8477
IP	6/7	5.63855	5.63715	.00327	25.64042			
9	6/7		3.82600	.00306	23.82906	18.1136	.2986	17.8150
IP	6/8	5.63819	5.63677	.00329	25.64006			
10	6/8		5.48987	.00326	25.49313	1.44693	.0207	1.4486
IP	6/12	5.63796	5.63656	.00327	25.63983			
11	6/12		4.95057	.00316	24.95373	6.8610	.1021	6.7589
12	6/12		5.16775	.00322	25.17097	4.6886	.0683	4.6203
IP	6/13	5.63847	5.63709	.00326	25.64035			
13	6/13		5.37138	.00322	25.37460	2.6575	.0378	2.6197
14	6/13		5.47725	.00324	25.48049	1.5986	.0225	1.5761
IP	6/14	5.63850	5.63710	.00327	25.64037			
15	6/14		4.82413	.00316	24.82729	8.1308	.1224	8.0084
16	6/14		4.99418	.00313	24.99731	6.4306	.0953	6.3353
17	6/14		5.13807	.00315	25.14122	4.9915	.0728	4.9187
IP	6/16	5.63798	5.63660	.00326	25.63986			
18	6/16		5.06531	.00319	25.06850	5.7136	.0841	5.6295
19	6/16		5.15216	.00324	25.15540	4.8446	.0707	4.7739
20	6/16		5.15218	.00324	25.15542	4.8444	.0707	4.7737
21	6/16		5.30838	.00321	25.31159	3.2827	.0471	3.2356
22	6/16		5.39925	.00321	25.40246	2.3740	.0338	2.3402

TABLE I--CONTINUED

$-E$	$E^2 \times 10^{-3}$	$-E^3 \times 10^{-5}$	$-1.11195 \times E$	$-1.5578 \times E^2 \times 10^{-2}$	$-0.5173 \times E^3 \times 10^{-5}$	$-t_E$	$t_P - t_E$	$\frac{t_P - t_E}{t_P}$
10.3971	.10810	.01124	11.56106	.16840	.00581	11.73527	.0056	.00048
10.3945	.10805	.01123	11.55816	.16832	.00581	11.73229	.0036	.00031
9.1818	.08421	.00773	10.20970	.13119	.00400	10.34489	.0031	.00029
7.1734	.05146	.00369	7.97646	.08017	.00191	8.05854	.0014	.00017
7.1583	.05124	.00367	7.95967	.07981	.00190	8.04138	.0000	.00000
4.0848	.01669	.00068	4.54209	.02600	.00035	4.56844	-.0030	-.00075
15.8486	.25118	.03981	17.62285	.39130	.02059	18.03474	.0010	.00001
15.6883	.24612	.03861	17.44461	.38342	.01997	17.84800	.0003	.00000
15.6574	.24515	.03838	17.41025	.38190	.01985	17.81200	-.0030	-.00017
1.29975	.00169	.00002	1.44526	.00263	.00001	1.44790	-.0007	-.00048
6.0176	.03621	.00218	6.69127	.05641	.00113	6.74881	-.0101	-.00144
4.1281	.01704	.00070	4.59024	.02655	.00036	4.61715	-.0031	-.00067
2.3517	.00553	.00013	2.61497	.00861	.00007	2.62365	.0040	.00151
1.4184	.00101	.000014	1.57719	.00157	.00001	1.57877	.0027	.00172
7.1312	.05085	.00363	7.92954	.07922	.00188	8.01064	.0022	.00027
5.6539	.03197	.00181	6.28685	.04980	.00094	6.33759	.0026	.00041
4.3953	.01932	.00084	4.88735	.03010	.00043	4.91788	-.0008	-.00016
5.0276	.02528	.00127	5.59044	.03938	.00066	5.63048	.0010	.00018
4.2276	.01820	.00078	4.74313	.02835	.00040	4.77188	-.0020	-.00042
4.2661	.01820	.00078	4.74369	.02835	.00040	4.77244	-.0013	-.00027
2.8961	.00839	.00024	3.22032	.01307	.00012	3.23351	-.0021	-.00065
2.0984	.00440	.00009	2.33332	.00685	.00005	2.34022	.0000	.00000

TABLE I--CONTINUED

Point No.	Date	R -20	N -20	C	R_0 or R_t	$-10(R_t - R_0)$	k'	$-t_p$
IP	6/21	5.63740	5.63994	.00330	25.63924			
23	6/21	5.20810		.00184	25.20994	4.2930	.0623	4.2307
IP	7/30	5.63827	5.63686	.00328	25.64014			
24	7/30		4.72131	.00317	24.72448	9.1566	.1393	9.0173
IP	7/30	5.63774	5.63630	.00329	25.63959			
25	7/30	5.23928		.00183	25.24111	3.9848	.0576	3.9272
IP	7/31	5.63782	5.63638	.00329	25.63967			
26	7/31		5.31477	.00325	25.31802	3.2165	.0460	3.1705
IP	8/4	5.63769	5.63620	.00331	25.63951			
27	8/4		5.49150	.00328	25.49478	1.4473	.0203	1.4270
28	8/4		5.53527	.00331	25.53858	1.0093	.0141	.9952
IP	8/11	5.63785	5.63644	.00328	25.63972			
29	8/11	5.02723		.00181	25.02905	6.1067	.0902	6.0155

Points Above Zero

Point No.	Date	R -20	N -20	C	R_0 or R_t	$10(R_t - R_0)$	k'	t_p
IP	7/9	5.63760	5.63616	.00329	25.63945			
30	7/9	6.12213		.00183	26.12396	4.8451	.0640	4.7811
IP	7/9	5.63752	5.63625	.00321	25.63946			
31	7/9		5.97183	.00318	25.97501	3.3555	.0443	3.3112
IP	7/12	5.63803	5.63662	.00327	25.63989			
32	7/12		6.10513	.00342	26.10855	4.6866	.0621	4.6245
33	7/12		6.33665	.00345	26.34010	7.0021	.0893	6.9128
34	7/12		6.61647	.00345	26.61992	9.8003	.1220	9.6783
IP	7/13	5.63792	5.63648	.00329	25.63977			
35	7/13	8.90478		.00221	28.90699	32.6722	.2988	32.3734
IP	8/10	5.63772	5.63630	.00328	25.63958			
36	8/10		6.48592	.00345	26.48937	8.4979	.1068	8.3911
37	8/10		6.72185	.00347	26.72532	10.8574	.1338	10.7236

TABLE I--CONTINUED

$-E$	$E^2 \times 10^{-3}$	$-E^3 \times 10^{-5}$	$-1.11195 \times E$	$-1.5578 \times E^2 \times 10^{-3}$	$-.5173 \times E^3 \times 10^{-5}$	$-t_E$	$t_p - t_E$	$\frac{t_p - t_E}{t_p}$
3.7854	.01433	.00054	4.20918	.02232	.00028	4.23178	.0011	.00026
8.0263	.06442	.00517	8.92484	.10036	.00267	9.02787	.0105	.00114
3.5144	.01235	.00043	3.90784	.01924	.00022	3.92730	-.0001	.00000
2.84274	.00808	.00023	3.16098	.01259	.00012	3.17369	.0032	.00101
1.2833	.00165	.00002	1.42697	.00257	.00001	1.42955	.0026	.00182
0.8930	.00080		0.99297	.00125		0.99422	-.0010	-.0010
5.36965	.02883	.00155	5.97078	.04491	.00080	6.01649	.001	.00017

Points Above Zero

E	$E^2 \times 10^{-3}$	$E^3 \times 10^{-5}$	$1.11195 \times E$	$1.5578 \times E^2 \times 10^{-3}$	$.5173 \times E^3 \times 10^{-5}$	t_E	$t_p - t_E$	$\frac{t_p - t_E}{t_p}$
4.3255	.018710	.00081	4.80974	.02915	.00042	4.78101	.0001	.00000
2.9952	.00897	.00027	3.33051	.01397	.00014	3.3167	-.0055	-.00168
4.18318	.01750	.00073	4.65149	.02726	.00038	4.62461	-.0001	-.0000
6.27133	.03933	.00247	6.97341	.06127	.00128	6.91342	-.0006	-.0001
8.81013	.07762	.00684	9.79642	.12092	.00354	9.67904	-.0007	-.0001
30.2515	.91515	.27686	33.6382	1.42566	.14321	32.35575	.0178	.0005
7.6257	.05815	.00443	8.47940	.09059	.00229	8.39110	.0000	.0000
9.7753	.09556	.00934	10.86864	.14886	.00483	10.72461	-.0010	-.0001

point vessel and also for the brine-ice mixture in the containing bath. The temperature of the latter was manually adjusted within a tenth of a degree of that inside the vessel.

The following empirical equation was derived to express the temperature, t , as obtained from the Callendar formula,²⁵ in terms of the electromotive force, E , in millivolts:

$$t = 1.11195 E - 1.5578 (10^{-3} E^2) + 0.5173 (10^{-5} E^3)$$

E is taken to be negative if the ice-solution side is colder than the reference side. The constants were roughly calculated first, then adjusted to the apparently best values by the use of a deviation plot. In Fig. 2 is shown the deviation plot for the final equation. It is seen that the average deviation is somewhat less than 0.05 per cent. Table I gives the data for this calibration, the steps in the calculation, and the values of $(t_p - t_E)/t_p$, where t_p is the platinum thermometer temperature, and t_E the temperature calculated by the calibration equation.

Both the resistance thermometer and the Mueller Wheatstone Bridge used to measure its resistance were calibrated by the United States Bureau of Standards, the latter at twenty-three degrees centigrade. Since the temperature control of the bridge is an important factor, an oil thermostat with a temperature control of $\pm 0.02^\circ$ was constructed to replace the unsatisfactory air thermostat which had been formerly used. The bridge was supported inside a copper box by a frame work attached to the heavy brass top, and the box was suspended in the thermostat. The dials were operated by rods which extended up through brass tubes to a second set of dials on a panel across the top of the thermostat. To test the effectiveness of this temperature control, the

²⁵Cf. Griffiths, "Methods of Measuring Temperature," Charles Griffin and Company, London, 1918, p. 31.

thermostat was made to operate at 19° for twelve hours before the resistance in ice, i.e., R_0 , was measured. The thermostat temperature was then changed to 23° and R_0 determined at intervals. In five hours it had become constant, and the total change in R_0 translated into degrees by the Callendar formula amounted to 0.01° . To obtain a precision of 0.0001° with the thermometer, according to the test, the temperature of the bridge should be $23.00^{\circ} \pm 0.05^{\circ}$. In practice the thermostat was operated at $23.00^{\circ} \pm 0.02^{\circ}$ for at least seven hours before measurements were made. Before each series of measurements the switch levers were run over the coil taps several times in order to insure good contact.

The difficulty noted by Urbain of keeping the balance of the two arms of the bridge seems to have been eliminated by the new arrangement for adjusting the slide wire mentioned at the beginning of this section. The balance was frequently checked but only two or three readjustments were necessary during the entire period of its use in this work.

IV. MEASUREMENT OF CONCENTRATION

The analysis.- To determine the concentration of a solution, its electrical conductance was measured, either directly or after dilution, in a cell²⁶ calibrated with fifteen standard solutions of hydrochloric acid. The cell was rinsed with the solution to be measured eight times before it was filled, placed in a thermostat operating at $25.00^{\circ} \pm 0.02^{\circ}$, allowed to come to the temperature of the thermostat, and the resistance reading recorded. Subsequent refillings were made until the resistance remained constant. The conductivity set-up was the same as that employed by Hartsuch.²⁷ No difficulty was experienced in

²⁶The same cell is described by Urbain, op. cit.

²⁷Hartsuch, Ph.D. Dissertation, University of Chicago, 1935.

obtaining check readings to 0.02 per cent when the cell was refilled. Usually the check was closer. The samples having concentrations below 0.29 molal were measured without dilution.

In the preparation of the standard solutions two stock solutions were first analyzed according to the method described in detail by Hartsuch,²⁸ and then diluted with the same technique employed for the freezing point samples. The data for the analyses, dilutions and resistance measurements are given in Tables II and III. The concentrations of the diluted standard solutions extended over a range which was approximately the same as that of the unknown solutions. Great care had to be exercised in all dilutions if the necessary precision was to be obtained. One step in the procedure needs special citation: The solution was always added to the weighed quantity of water, instead of water to the acid. Some acid seemed to be lost as spray when the reverse procedure was followed. Small pyrex flasks, stoppered with paraffined corks, and capable of being weighed on a balance sensitive to 0.1 mg. were employed.

The following linear equation was found to express the resistance, R , as a function of the molality, M .

$$1/MR = -0.0109867 (1/\sqrt{R}) + 0.00270007$$

The deviation, ϵ , of each calculated value of $1/MR$ from that found is shown in Fig. 3. The two symbols are employed to distinguish the deviations for the standards made from different stock solutions. The largest deviation is approximately 0.05 per cent of the $1/MR$ value, and the random distribution did not justify a correction when the equation was employed in the analysis of a freezing point sample.

²⁸Ibid.

TABLE II

ANALYSIS OF STOCK SOLUTIONS
(WEIGHTS ARE IN GRAMS)

Solution Number	1	1	1	2	2
Burette plus sample	69.0763	49.3369	43.4390	50.5086	49.2927
Burette minus sample	<u>61.5920</u>	<u>43.4390</u>	<u>38.0989</u>	<u>49.2927</u>	<u>48.0112</u>
Sample in air	7.4843	5.8979	5.3401	1.2159	1.2815
Vacuum correction	<u>.0073</u>	<u>.0061</u>	<u>.0055</u>	<u>.0012</u>	<u>.0012</u>
Sample (vac.)	7.4921	5.9040	5.3456	1.2171	1.2827
Crucible plus AgCl	5.9553	1.4587	2.2596	4.6716	3.8185
Crucible	<u>4.6717</u>	<u>.4479</u>	<u>1.1444</u>	<u>3.7034</u>	<u>2.7983</u>
Silver Chloride in Air	1.2836	1.0108	.9152	.9682	1.0202
Vacuum correction	<u>.0001</u>	<u>.0001</u>	<u>.0001</u>	<u>.0001</u>	<u>.0001</u>
AgCl (vac.)	1.2837	1.0109	.9153	.9683	1.0203
HCl	.32657	.25717	.23285	.24634	.25956
Water	7.16555	5.64683	5.11275	.97076	1.02314
Molality	1.24983	1.24893	1.24895	6.95900	6.95706

TABLE III

DILUTIONS OF STOCK SOLUTIONS TO MAKE STANDARD SOLUTIONS AND CALIBRATION OF THE CONDUCTIVITY CELL

Sol. No.	Weight H ₂ O	Weight Sol'n	Molality	Resistance	1/MR	(1/MR)'	ε
1	78.5279	6.0696(1)	.085979	4583.0	.00253778	.00253778	+.050,00
2	95.9703	7.3142(1)	.084847	4642.6	.00253868	.00253882	-.050,14
3	71.4088	5.4882(1)	.085521	4608.9	.00253705	.00253824	-.051,21
4	98.1201	9.8845(1)	.10976	3619.4	.00251717	.00251745	-.050,28
5	78.8319	10.0605(1)	.13586	2946.7	.00249782	.00249768	+.050,14
6	98.1676	5.6455(1)	.065115	6002.5	.00255852	.00255822	+.050,26

TABLE III--CONTINUED

Sol. No.	Weight H ₂ O	Weight Sol'n	Molality	Resistance	1/MR	(1/MR)'	ε
7	97.6776	30.4607(1)	.28693	1445.5	.00241109	.00241109	.050,00
8	98.5569	15.5970(1)	.16419	2456.8	.00247906	.00247841	+.050,65
9	96.3809	4.4543(2)	.24737	1663.1	.00243065	.00245067	-.050,02
10	276.697	3.9805(2)	.078933	4877.6	.00256518	.00254435	+.050,83
11	282.843	6.2274(2)	.12008	3317.1	.00251052	.00250931	-.051,21
12	48.2774	1.5531(2)	.17407	2323.8	.00247209	.00246216	-.050,07
13	48.3994	1.2146(2)	.13654	2934.1	.00249604	.00249724	-.051,20
14	311.411	5.6757(2)	.09970	3970.8	.00252591	.00252572	+.050,19
15	354.342	9.0798(2)	.139363	2875.1	.00249572	.00249517	+.050,55

Materials and sources of impurities.- Distilled water was added to the best grade of laboratory hydrochloric acid²⁹ to make it approximately 20.2 per cent, and this solution was distilled in an all glass apparatus. The middle third which was nearly a constant boiling mixture was retained for redistillation within twenty-four hours preceding a freezing point determination.

The laboratory distilled water was found to be of sufficient purity for this work. Its specific conductance was 2×10^{-6} reciprocal ohms. Several workers³⁰ have noted that clear commercial ice was very pure. Its use was adopted since the conductance of the water, obtained by the melting of a sample of ice prepared as for a freezing point determination, indicated the ice to be approximately as pure as the distilled water.

Pyrex glass was used for all the hydrochloric acid

²⁹Baker and Adamson's C. P. Reagent Quality.

³⁰Hall and Harkins, J. Am. Chem. Soc., 38, 2658 (1916); Randall and Vaneslow, J. Am. Chem. Soc., 46, 2418 (1924).

containers. To learn something of its effect on the solutions, the conductivities of several of these were measured after they had been allowed to stand for four days. They showed no appreciable change. Robertson and LaMer³¹ found that the equivalent of 0.000018 mol./liter of potassium chloride went into solution when a solution of potassium chloride was allowed to stand in a pyrex flask over a period of several days. In our experiment there may have been an exchange of hydrogen ions for sodium or potassium ions, but the net effect was not detectable. To avoid errors in the freezing point determinations due to a slow reaction with the glass not more than four days, usually but one or two days, were allowed to elapse between the distillation of the acid and the final conductance measurements. The probability of an appreciable error in the calibration of the conductance cell due to glass solubility was shown to be very small in the following way: Four of the standard solutions were made from stock solution number one after it had been allowed to stand in a pyrex flask for two weeks. The deviations calculated for these were random.

The removal of an appreciable amount of hydrochloric acid by adsorption could not be detected by a difference in conductance before and after a transfer from one flask to another. This effect probably does not become noticeable until lower concentrations are reached.

The purification of the air stream has already been discussed, and an introduction of impurities from this source is highly improbable.

The cleaning procedure for the dewars, stirrers, flasks, and pipettes included a warm nitric acid treatment, twenty-five rinsings with tap water and ten with boiling hot distilled water.

³¹Robertson and LaMer, J. Phys. Chem., 35, 1953 (1931).

The flasks and pipettes were dried by warm dry air drawn through them; the air was dried with calcium chloride and the dust was thoroughly removed by a cotton-wool filter eighteen inches long.

V. PROCEDURE

Clear commercial ice was prepared for the dewars as follows: It was pounded through a cast iron mesh; the finely crushed portion was washed away so that pieces of approximately one-half inch diameter remained; this was rinsed twice with distilled water. About 250 grams were transferred to each dewar and stirred well with distilled water which had been precooled to zero centigrade. The water was siphoned off and to one dewar more of this precooled water was added, to the other, acid solution precooled almost to its freezing point in brine-ice mixture.

When the freezing points of the more concentrated solutions were determined, it was necessary to precool the ice in the acid dewar. This was done as follows: The vessel was filled to the top with ice, this mixed with precooled acid, then the liquid siphoned off before more precooled acid was added. The lowest desired temperature was reached easily in this way. The levels in the dewars were adjusted so that they would come almost to the top of the glass pump-cylinders after they were lowered into place, and the relative amounts of ice and liquid were such that the hand stirrers could be moved from top to bottom without the exertion of much force. It was found by experiment that the ratio of ice to liquid could be decreased considerably without any apparent effect on the measured equilibrium temperature, provided the thermostat temperature was kept within 0.5° of the inside temperature.

Great care had to be exercised when the top, with its attached glass parts, was lowered to the dewar cases, since the

glass cylinders could not stand much lateral strain. The upper part was supported with one hand while the wire stirrers were operated alternately with the other. For the more concentrated solutions it was also necessary to work the pump stirrer in the ice-solution side during this operation, otherwise the valves would stick due to the re-freezing of the ice melted by the warmer glass parts.

After the apparatus was in place, in the double thermostat, the zero and sub-zero sides of the latter were filled with ice and a mixture of calcium chloride and ice, respectively. The temperature of the sub-zero side was adjusted until it was about one degree colder than the dewar contents, and the pump stirrers started at the rate of sixty strokes a minute. After three minutes, the water in the reference dewar was siphoned off (the pump was stopped while ice only remained), and an equal volume of water cooled to zero degrees introduced. This procedure has been recommended by White³² in his directions for obtaining a reproducible triple point for ice, air, and water.

The pipette employed had a special shape which allowed the temperature of the water to be maintained at approximately zero degrees during the transfer. The pipette bulb remained in the ice bath and the delivery tube arched upward from the lower end of the bulb in the shape of an inverted U. Rapid siphoning was permitted. The tip passed through the connecting tube J (Fig. 1) into the mouth of the dewar. To start the siphon air pressure was applied to the upper end of the pipette through a soda-lime tube. The water to be transferred was initially cooled to zero degrees in a brine-ice mixture.

³²White, J. Am. Chem. Soc., 56, 20 (1934).

The air stream was started through both vessels at the rate of 100 cubic centimeters per minute, but after fifteen minutes the rate was reduced to 30 cubic centimeters per minute and continued at that rate until just before the sample was withdrawn. A constant temperature was established by this time except for the solutions near four molal. For these solutions the bath temperature could not be maintained to match that in the freezing point vessel. The principal test for an equilibrium state was to compare electromotive force measurements made before and after manipulation with the hand stirrers and a double-tempo pump stirring. No change, or a very small change indicated a steady state. Tests with the platinum thermometer showed that the temperature in the reference side remained constant over a period of two or three hours with pump stirring only. Over longer periods, however, the ice tended to form a solid mass, and sometimes a slight temperature drop was noted after the mass had been broken with the wire stirrer.

The procedure for taking samples when the apparatus had reached a steady state was as follows: (1) the air tube on the ice-solution side was transferred to the upper end of the sampling pipette. The tip of the pipette was inserted into the freezing point vessel to a depth previously determined. In this position the tip was opposite the central portion of the thermel junctions. No liquid entered because of the air stream passing through it. (2) Regular stirring proceeded for five minutes; then, if a hand stirring and a double-tempo pump stirring produced no appreciable temperature change, or in concentrated solutions was followed by a very slow drift, regular stirring was continued for another two minutes, and an electromotive force reading recorded.

Approximately seventy cubic centimeters of acid were now

withdrawn from the equilibrium mixture. To do this, the air tube was replaced by a tube connected to an ordinary filter pump which was already operating. This sample was transferred immediately afterward to an Erlenmeyer flask, having a capacity of 125 cubic centimeters. Another electromotive force reading immediately followed. Even in the most concentrated solutions the two freezing point lowerings did not differ more than 0.02 per cent.

The solution thus removed was replaced by an equal quantity of water at zero degrees. However, it was necessary to add the water very slowly. Otherwise, the valves in the pump stirrer would stick. The temperature of the containing bath was now readjusted to match that inside the dewar; the air stream passed again into the ice solution mixture; and after a ten minute period, the test for an equilibrium mixture made. Four or five freezing points could usually be obtained with one charge of ice.

Errors in sampling.- Transference of the solution to the flask could entail serious errors. Moisture condenses on the tip during the exposure to the air, and the subsequent introduction of this into the flask along with the solution could change the concentration one or two tenths of a per cent. Our procedure was to place a good grade of filter paper over the top of the receiving flask and bend it downward around the lip. The wet tip would easily puncture this but, to all appearances, leave the condensed moisture on the paper which acted as a blotter. To test the effectiveness of this precaution, the conductance of a sodium chloride solution was measured before and after it was transferred by means of the sampling pipette from a flask at -10° C. to another flask at room temperature. When the paper was used no appreciable difference in the two conductance measurements was observed. Once, when the paper was not used, a difference was observed. Two other

functions of the paper were to hold the tip away from the walls, and to prevent air from circulating down and leaving some additional moisture. This last possibility did not cause an appreciable error in our work as shown by a simple test: A standard solution was chilled to -10°C . and then left open about fifteen minutes, or until it warmed to room temperature. This was on a moderately humid day. Its concentration did not change as indicated by a resistance measurement.

Evaporation into the upper part of the flask could cause a decrease in concentration of about 0.002 per cent if the air in it initially was very dry. Under certain conditions, however, relatively large amounts of water distilled onto the upper walls. To prevent an error from entering into a determination in this way, each flask was always shaken before any of its contents was poured into the conductance cell.

VI. THE RESULTS

The calculation of the molalities of the samples, m , the freezing point depression, θ , and the corresponding j values are given in Tables IV, V, and VI, respectively. The plot of j versus $\log. M$ in Fig. 4 serves to compare our values with those of Roloff.³³ Jones and Bassett³⁴ have reported freezing point measurements in the range from one to four molal, but they employed the faulty super-cooling technique and their values were erratic. Roloff's values are the most consistent of any reported previously in this range. The check between our values and those of Randall and Vanselow³⁵ and Chadwell³⁶ is also indicated.

³³Roloff, Z. Physik, Chem., 18, 572 (1895).

³⁴Jones and Bassett, Am. Chem. J., 34, 290 (1905).

³⁵Randall and Vanselow, loc. cit.

³⁶Chadwell, loc. cit.

TABLE IV

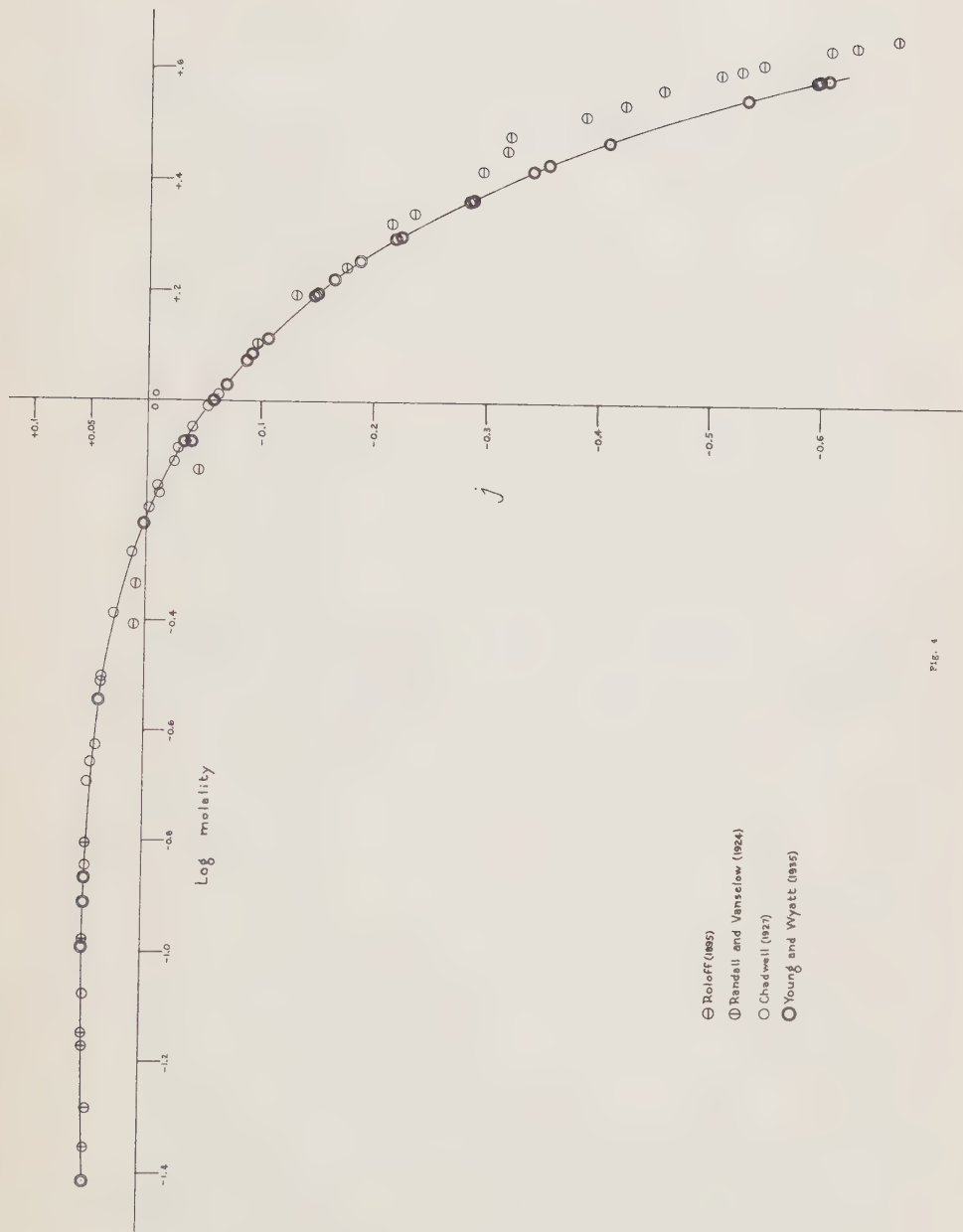
Pt. No.	E	E^2 $\times 10^{-3}$	E^3 $\times 10^{-5}$	1.11195 $\times E$	1.5578 $\times E^2 \times$ 10^{-3}	$.5173$ $\times E^3$ $\times 10^{-5}$	η
1	.12152	.000018		.13512	.00002		.13514
2	.32045	.00010		.35632	.00016		.35648
3	.38412	.00015		.42710	.00023		.42733
4	.42638	.00018		.47414	.00028		.47442
5	1.2979	.00168	.00002	1.4432	.00262	.00001	1.44583
6	4.40465	.019401	.00085	4.89775	.03022	.00044	4.92841
7	1.97965	.00392	.00008	2.20127	.00611	.00004	2.20742
8	12.03850	.14493	.01745	13.38621	.22577	.00903	13.62101
9	9.90886	.09819	.00973	11.01816	.15296	.00503	11.17615
10	8.07776	.06525	.00527	8.98207	.10165	.00273	9.08645
11	5.89327	.03473	.00205	6.55302	.05410	.00106	6.60818
12	3.80185	.01445	.00055	4.22747	.02252	.00028	4.25027
13	20.40611	.41641	.08497	22.69056	.64870	.04396	23.3832
14	6.38496	.04077	.00260	7.09976	.06351	.00135	7.16462
15	5.380887	.03458	.00203	6.53923	.05388	.00105	6.59416
16	4.26589	.01820	.00078	4.74346	.02835	.00040	4.77221
17	3.51779	.01237	.00044	3.91161	.01928	.00023	3.93112
18	2.89952	.00841	.00024	3.22412	.01310	.00012	3.23734
19	20.2691	.41084	.08327	22.53823	.64002	.04308	23.2213
20	20.1580	.40634	.08191	22.41470	.63302	.04237	23.09008
21	17.9443	.32200	.05778	19.95316	.50162	.02989	20.48467
22	7.99859	.06398	.00512	8.89403	.09967	.00265	8.99635
23	7.06580	.04993	.00353	7.85682	.07778	.00183	7.93642
24	5.99092	.03589	.00215	6.66160	.05591	.00111	6.71862
25	4.77237	.02278	.00109	5.30664	.03548	.00056	5.34268
26	13.8063	.19061	.02632	15.35192	.29695	.01362	15.66249
27	11.6170	.13495	.01568	12.91752	.21024	.00811	13.13587
28	9.8693	.09740	.00961	10.97417	.15174	.00497	11.13088

TABLE V

Pt. No.	Weight H ₂ O	Weight Sol'n	Resistance	M'	M
1			10113.0		.038167
2			3914.0		.101207
3			3290.4		.121152
4			2974.8		.134538
5			1461.94		.293505
6	72.4801 67.3642	10.1580 10.1649	2790.22 2621.10	.143814 .153500	1.21545 1.21587
7	65.1130 69.7512	10.1878 10.2063	4970.20 5258.63	.078081 .074616	.595483 .59563
8	78.7747	5.8613	2355.09	.171652	2.70628
9	61.3188	6.0527	2087.25	.194789	2.33626
10	71.9542	5.9254	2817.45	.142366	1.99706
11	98.7196	10.1701	2907.47	.137780	1.55082
12	79.3631	10.5834	3274.13	.121777	1.07061
13	96.4810	5.0880	2337.75	.172984	3.92236
14	97.7823	10.1229	2724.65	.147422	1.65752
15	101.5088	10.0240	3018.76	.132453	1.54954
16	73.7198 75.9717	9.9787 9.8932	2945.35 3044.49	.135936 .131335	1.18353 1.18340
17	72.0042	10.0538	3352.27	.118832	1.00096
18	88.1837	15.8730	3199.77	.124718	.83879
19	96.5328	5.5177	2176.52	.186421	3.91328
20	97.0063	5.9179	2057.66	.197728	3.89980
21	84.9756	5.7469	2007.64	.202901	3.59851
22	100.3114	10.3782	2316.46	.174647	1.98489
23	96.3368	10.2338	2474.10	.163032	1.79839
24	93.1474	10.0993	2745.55	.146252	1.57250
25	91.0756	10.1187	3197.90	.124793	1.30132
26	96.9289	6.9898	2218.26	.182749	2.99360
27	95.0698	6.7835	2501.30	.161181	2.63735
28	97.0304	6.9433	2780.44	.144341	2.33307

TABLE VI

Date	Pt. No.	M	2 M λ	$\mathcal{J}/2M\lambda$		j	log. M
8/19	1	.0381665	.141888	.13514	.95244	+.04756	-1.4183
8/19	2	.101207	.376247	.35648	.94746	+.05254	- .9948
8/19	3	.121152	.450395	.42733	.94879	+.05121	- .9167
8/19	4	.134538	.500158	.47442	.94854	+.05146	- .87115
8/19	5	.283505	1.05396	1.01393	.95917	+.040827	- .5475
8/25	6	1.21560	4.51911	4.92841		-.09057	.0846
8/25	7	.59556	2.21405	2.20742	.99701	+.00299	- .2250
8/30	8	2.70628	10.06086	13.62101		-.35386	.4323
8/30	9	2.33626	8.68528	11.17615		-.28679	.3685
9/1	10	1.99706	7.42427	9.08645		-.22388	.3004
9/1	11	1.55082	5.76533	6.60818		-.14619	.1906
9/1	12	1.07061	3.98010	4.25027		-.06788	.0294
9/5	13	3.92236	14.58177	23.38322		-.60359	.5935
9/6	14	1.65752	6.16200	7.16462		-.16271	.2196
9/6	15	1.54954	5.76057	6.59416		-.14471	.1903
9/6	16	1.18346	4.39963	4.77221		-.08468	.0730
9/6	17	1.00096	3.72117	3.93112		-.05642	.0004
9/6	18	.83879	3.11829	3.23734		-.03817	-.0763
9/8	19	3.91328	14.5480	23.22133		-.59619	.5925
9/8	20	3.89980	14.4979	23.09008		-.59265	.5911
9/8	21	3.59851	13.3778	20.48467		-.53124	.5562
9/9	22	1.98490	7.38148	8.99635		-.21877	.2980
9/9	23	1.79839	6.68570	7.93643		-.18708	.2548
9/9	24	1.57250	5.84593	6.71862		-.14911	.1967
9/9	25	1.30132	4.83779	5.34268		-.10436	.1143
9/12	26	2.99360	11.12901	15.66249		-.40736	.4763
9/12	27	2.63735	9.80461	13.13587		-.33976	.4211
9/12	28	2.33307	8.67342	11.13088		-.28333	.3879



- ⊖ Toloff (1935)
- ⊕ Randall and Vanselow (1924)
- Chadwell (1927)
- Young and Wyatt (1935)

Fig. 4

TABLE VII

EXAMPLE

Dilution of Sample taken for Point Number 7	(a)	(b)
Flask plus solution	24.4409	23.1337
Flask	<u>14.2934</u>	<u>12.9793</u>
Solution	10.1475	10.1544
	<u>.0105</u>	<u>.0105</u>
W ₁ : Wt. of Solution (vac.)	10.1580	10.1649
Flask plus solution plus water	96.8442	90.4276
Flask plus solution	<u>24.4409</u>	<u>23.1337</u>
Water	72.4033	67.2939
	<u>.0768</u>	<u>.0703</u>
W ₂ : Wt. of water (vac.)	72.4801	67.3642
Calculation of Molality of Sample: M, (Using the resistance of the above solutions in a conductivity cell, the calibration equation of which is $1/M'R = -0.0109867 (1/\sqrt{R}) + 0.00270007$, M', the Molality of the diluted solution is first calculated, then, from the above data, M is calculated.)		
R	2790.22	2621.10
$\sqrt{R}$	52.8225	51.1967
$1/\sqrt{R}$	.0189313	.0195325
$0.0109867 (1/\sqrt{R})$	.00020799	.000214597
$1/M'R$	.00249208	.00248547
$1/M'$	6.95345	6.51467
M'	.143814	.153500
W ₁ - W ₂	82.6381	77.5291
W ₁ /M'	70.6329	66.2208
$0.036465 W_2$	2.64299	2.45644
$(W_1/M') - 0.035465 W_2$	67.9899	63.7644
$M = (W_1 - W_2)/(W_1/M' - 0.035465 W_2)$	1.21545	1.21587

Mean: 1.2156

When heats of dilution data are available for the calculation of activity coefficients by the freezing point method, a comparison with the activity coefficients calculated from electromotive force measurements will probably constitute the most rigorous test to which these methods will have been subjected. The chief limitations have been: (1) for the freezing point method, a lack of sufficiently good thermal and freezing point depression data; (2) for the e.m.f. method, the effect of silver chloride solubility in the more concentrated hydrochloric acid solutions.

To demonstrate the effect of the new hydrochloric acid freezing point data, a calculation of the provisional values of the activity coefficients, γ' 's, so called by Lewis and Randall,³⁷ when the heats of dilution are neglected, will serve. The ratio $\gamma'/\gamma'_{0.1}$ is calculated by using the following equation, where the symbols and numerical values for the constants are those employed by T. F. Young.³⁸

$$\log \frac{\gamma'}{\gamma'_{0.1}} = - \int_{0.1}^m j d \log m - \frac{j_m - j_{0.1}}{2.3026} + \frac{B_2}{V} \int_{0.1}^m \frac{g}{m} d(g) + \frac{C_2}{2V} \int_{0.1}^m \frac{g}{m} d(g^2)$$

The values of j listed in Table VIII were read from a plot sufficiently large to make full use of the precision of the data. The g 's in the third column are calculated from these j 's, and those in the fourth are calculated by Randall and E. Young.³⁹ The calculation of the ratio $\gamma'/\gamma'_{0.1}$ is shown in detail in

³⁷ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 341.

³⁸ T.F. Young, Chem. Rev., 13, 103 (1933).

³⁹ Randall and E. Young, loc. cit.

Table IX. The last two columns contain a comparison with the values of Randall and E. Young. The difference is largely accounted for by the difference in the ϑ 's employed.

TABLE VIII

m	j	ϑ	ϑ R and Y
0.1	.0517	.35254	.35209
0.2	.0502	.70620	.7064
0.5	.0144	1.8320	1.8225
1.0	-.0562	3.9265	3.5172
2.0	-.2217	9.0836	
3.0	-.4085	15.7087	
4.0	-.6250	24.1638	

TABLE IX

m	$-\int_{\vartheta_1}^m j d \log m$	$\frac{j_m - j_{\vartheta_1}}{2.3026}$	$\int_{\vartheta_1}^{\vartheta_2} \frac{\vartheta}{m} d(\vartheta)$	$\int_{\vartheta_1}^{\vartheta_2} \frac{\vartheta}{m} d(\vartheta^2)$	$\log \gamma/\gamma_1$	γ/γ_1	γ/γ_1 R and Y
0.1	.00000	.00000	.00000	.00000	.00000		
0.2	-.01542	.00065	.000149	.000002	-.01462	.9669	.9667
0.5	-.03025	.01620	.000633	.000017	-.01340	.9696	.9643
1.0	-.02394	.04686	.001582	.000085	.02459	1.0583	1.0476
2.0	.01423	.11873	.004191	.000524	.13767	1.3730	
3.0	.06935	.19986	.008060	.001730	.27900	1.9010	
4.0	.13280	.29389	.013755	.004584	.44503	2.7863	

In Table X the values of γ/γ_1 found in this investigation are compared with like values calculated from the freezing point depressions of Roloff.⁴⁰ Since the discrepancy amounts to about

⁴⁰Roloff, loc. cit.

3 per cent at two molal, 10 per cent at three molal, and 15 per cent at four molal, it is now apparent that activity coefficients from freezing points comparable with those from electromotive force data could not have been calculated heretofore even if the thermal data had been available.

TABLE X

m	log. γ'/γ'_{∞}	γ'/γ'_{∞}	γ'/γ'_{∞} (Roloff)
1	0.00000	0.0000	0.000
2	0.11308	1.2974	1.265
3	0.25441	1.7964	1.632
4	0.42044	2.6330	2.239

APPENDIX

List of Special Apparatus

White Potentiometer, Leeds and Northrup Company, No. 112177.

Type HS Galvanometer, used in conjunction with the White Potentiometer, Leeds and Northrup Company, No. 196145.

Resistance Thermometer, Leeds and Northrup Company, No. 103770.

Mueller Wheatstone Bridge, Leeds and Northrup Company, No. 57347.

Type HS Galvanometer, used in conjunction with the Mueller Bridge, Leeds and Northrup Company, No. 179715.

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